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Title page

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Synthesis and Characterization of Surrogate Nuclear Explosion Debris: Urban Glass Matrix

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Abstract

Surrogate nuclear explosive debris was synthesized and characterized for major, minor, and trace elemental composition as well as uranium isotopics. The samples consisted of an urban glass matrix, equal masses soda lime and cement, doped with 500 ppm uranium with varying enrichments. The surface and cross section morphology were measured with SEM, and the major elemental composition was determined by XPS. LA-ICP-MS was used to measure the uranium isotopic abundance comparing spot, line scans, and depth profiling sampling techniques. A fraction of each sample was leached and solution ICP-MS was performed to compare accuracy and precision of isotopic measurements to LA-ICP-MS results. The results provide an example of the application and utility of LA-ICP-MS for forensics applications.

Keywords

Surrogate Nuclear Explosive Debris, Uranium, Urban Matrix, Isotope Ratio, Fallout

Introduction

Post-detonation nuclear forensics uses the physio-chemical processes associated with a nuclear detonation to identify the device type and the source of the nuclear material in the device [1]. After a nuclear detonation, several key questions need to be answered to provide the decision makers with the necessary information to protect and serve the community at risk. The Joint Working Group of the American Physical Society and the American Association for the Advancement of Science have detailed a general timeline of the pertinent questions that need to be answered [2]. The yield of the detonation, general sophistication of the device, whether the device was primarily uranium or plutonium, and isotopic composition of fuel components all factor in to provenance determination and device design reconstruction.

During a nuclear detonation, the weapon and environment surrounding the detonation are melted and vaporized [3]. Surface detonations melt environmental material that can then either remain in place or be incorporated into the nuclear fireball. As the fireball cools, the device debris and environmental material are mixed into fused glassy material known as nuclear explosive melt debris [4]. There are two main types of nuclear explosive melt debris: ground glass and aerodynamic fallout [5]. The nuclear explosive melt debris is mainly composed of the displaced environment, and the device debris is present only in trace quantities [1]. For this reason, it is important to understand the local environment in the case of an urban detonation. The major components of buildings in cities are glass, steel and concrete. Glass and steel elemental compositions are fairly consistent in construction materials. Concrete consists of many components depending on the desired properties, where the elemental composition can vary significantly. Nominally, concrete contains cement, chemical admixtures and aggregates [6]. The cement and aggregates contain trace elements that may interfere with post-detonation nuclear forensics.

The formation of surrogate nuclear exposive debris (SNED) is of interest to the nuclear forensic community for training, method development of analytical techniques, and measurement exercises. The SNED material allows for laboratories to practice efficiency of answering relevant questions in a post-detonation scenario since nuclear explosive melt debris is limitied in quantity and accessibility. The shortage of nuclear explosive melt debris is due to the fact that testing was suspended in agreement with the

Comprehensive Nuclear-Test-Ban Treaty. In recent years, a variety of approaches to synthesize SNED materials have been published [7-11]. Each technique attempts to replicate and answer different characteristics of complex, inhomogenous nuclear explosive melt debris. The heat sources range from high power lasers [7, 8], electric arc [9], to furnaces [10, 11] in attempts to fuse the materials to mimic either the ground glass or aerodynamic fallout physical and chemical characteristics. The chemical matrices used in SNED range from NIST certified reference standards [7], borosilicate glass doped with highly enriched uranium (HEU) [11], to 50:50 combination of cement and soda lime doped with Xe [8]. In this work, SNED samples were prepared using soda lime and Portland cement to mimic an urban detonation. The SNED material is then doped with different enrichments of uranium to determine if the matrix would interfere with uranium isotopic analysis, and what elements can be expected to remain in nuclear explosive melt debris after an urban detonation.

The International Atomic Energy Agency (IAEA) has listed common analytical techniques used in nuclear forensic analysis [12]. These techniques are categorized based on elemental and isotopic bulk analysis, imaging, and microanalysis. Most of the techniques listed for elemental and isotopic analysis require lengthy digestion and seperations prior to analysis, this sample preparation leads to a delay in the key questions needed to be answered following a post-detonation scenario [12]. Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) as a nuclear forensic technique would minimize the number of steps in the handling process, maximizing throughput and turn-around time relative to current non-destructive assay techniques with the ability to determine isotopic composition and concentrations of elements of interest in nuclear explosive debris. LA-ICP-MS has the ability to measure bulk or local analysis with high spatial resolution of trace and isotopic analysis depending on the sampling technique (ie: spot, line scan, and depth profiling). The second portion of this work compares the different laser ablation sampling techniques to solution ICP-MS analysis to determine the viability of using LA-ICP-MS in a post-detonation scenario on a complex matrix.

Experimental

Sample Preparation

The main components of the urban glass matrix SNED samples were modeled after the World Trade Center debris, which composed of glass and concrete from the buildings [7]. Therefore, the SNED samples prepared consisted of a 50:50 mixture of soda lime and cement. The soda lime was purchased from Sigma-Aldrich and contained 75.2% SiO_2, 11.2% $CaCO_3$, 13.7% Na_2CO_3. The cement was purchased from Quikrete and contains Portland cement, silica sand, lime, limestone, iron oxide pigment and clay. The SNED samples were doped with 500 ppm of U_3O_8 with ^{235}U isotope concentrations of 0.72 (natural), 20, 50, and 80% ^{235}U. The 20 and 80% enriched $^{235}U_3O_8$ materials were purchased from New Brunswick Laboratory as NBL CRM standards. The 50% enriched U_3O_8 material was prepared in the laboratory, as described in the supplemental section. The total mixture of 50:50 soda lime:cement and the U_3O_8 powder was vortexed for 1 minute, then placed in a 5% Rh:Pt or 5% Au:Pt crucible. The samples were then heated under argon atmosphere at 1500 ˚C for 1 hour. The theoretical concentration of uranium in the melt glass was found to be 506.1 ± 43.3 ppm, determined by the amount added to the powder mixture prior to heating. A second set of doped uranium glass samples were prepared by Lawrence Livermore National Laboratory (LLNL) [13]. These samples were used as standards to quantify the amount of uranium in the blank SNED sample. The samples were doped with 5, 50, and 500 ppm natural uranium.

Scanning Electron Microscope/Energy Dispersive X-ray Emission Spectroscopy

Analysis of the surface and cross section morphology of the SNED samples was performed using a Scanning Electron Microscope (SEM). The JEOL JSM-6360LV SEM was equipped with a secondary electron and backscatter electron detectors. The natural uranium SNED sample was broken into pieces and mounted on copper tape. After mounting, the sample was sputter coated with palladium gold alloy to avoid charging on the surface, since the sample is non-conductive. The samples included a cross section, top, and bottom portion of the material. The images were collected using secondary electron imaging mode with an accelerating voltage of 20 kV and a working distance of

11 mm. The SEM also has the capability to measure elemental analysis through energy dispersive x-ray emission spectroscopy (EDS) using INCA mapping software. The elemental mapping was used to correlate the XPS data collected. For the EDS analysis, x-ray energies of 0 to 10 keV were detected.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was used to determine the bulk elements in the urban matrix glass materials. XPS data was collected using a Physical Electronics VersaProbe II system with a base pressure below 1 x 10^{-7} Pa. A variable-size, monochromated Al K_α x-ray source (1487 eV) was used throughout, and photoelectrons were energy sorted using a hemispherical analyzer. The XPS spectra are reported in terms of binding energy (BE) and instrument calibration was performed in accordance with ASTM procedure. Elemental composition was determined using survey scans at a pass energy of 117 eV. A pass energy of 29 eV was used for high-resolution scans to determine chemical valence state. Depth profiling was carried out using 2 kV argon ions. Charge neutralization for insulating samples is accomplised by focusing low energy ions and electrons at the spot of x-ray impingement. The blank SNED sample was crushed into two pieces and mounted on carbon tape. The samples were sputtered for 10 minutes prior to analysis to exclude any surface contamination. This sputtering time is estimated to drill several hundred angstroms into the sample.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

Analysis was conducted using LA-ICP-MS to determine the isotope ratio of the uranium and the trace constituents of the SNED samples. The laser ablation was an Electro Scientific Industries (ESI) New Wave Research (NWR) 213 Laser Ablation system equipped with a Nd:YAG deep UV (213 nm) laser was used for the analysis. The NWR 213 was coupled to a Thermo Scientific iCAP Q ICP-MS. Helium carrier gas was used to deliver the ablated material to the ICP-MS at a flow rate of 1 $Lmin^{-1}$. Prior to analysis ICP-MS parameters were optimized using NIST 612 glass. Three different sampling techniques were performed in order to characterize the material for homogeneity. The first analysis determined uranium isotopic homogeneity of the surface using laser

sampling of four randomly chosen areas of the sample with stationary laser spots. The second analysis, depth profile, verified uranium isotopic homogeneity of the samples in regards to depth. The depth profile analysis was conducted by drilling down into the sample with sequential laser shots, decreasing in spot size from 110 μm to 40 μm in increments of 10 μm for a total of 8 samplings per area. This procedure was repeated for a total of three times per sample for standard deviation calculations. The third laser sampling technique used line scan analysis, where the scan speed of the laser was set at 5 $\mu msec^{-1}$. Mass scan surveys were conducted on the 20% enriched $^{235}U_3O_8$ SNED sample to qualitatively determine trace elements in the matrix. Line scan analysis was used as the sampling technique in the mass scan surveys and the quantification of uranium in the blank SNED sample. The laser fluence, repitition rate and plasma power were held constant for all sampling techniques at 2 Jcm^{-2}, 20 Hz, and 1550 W. The parameters that varied for each type of analysis are listed in Table 1. The samples were probed for the isotopic abundace of ^{234}U, ^{235}U, ^{236}U, and ^{238}U. The dwell time of the ICP-MS using in laser ablation mode was 50 ms for all isotopes evaluated.

Table 1 Instrument parameters for solid (LA-ICP-MS) and solution (ICP-MS) analysis

Instrument Parameters	Mass Scan Survey LA-ICP-MS	Quantification LA-ICP-MS	Depth Profile LA-ICP-MS	Spot Analysis LA-ICP-MS	Line Scan LA-ICP-MS	Solution ICP-MS
Spot size (μm)	85	85	varied	85	85	n/a
Duration of ablation (s)	90	30	5	5	30	n/a
Dwell time (ms)	50	50	50	50	50	varied
Ar Nebulizer gas flow ($Lmin^{-1}$)	0.613	0.5193	0.635	0.586	0.596	0.9093
Integration time (s)	n/a	30	20	20	30	n/a
Sample size (n)	3	3	24	4	3	5

To compare the accuracy and precision of laser ablation to solution phase analysis, a portion of the SNED samples were gently crushed for leaching experiments. The small fractions of the crushed SNED samples, (masses listed in Table 2) were placed in 0.5 mL

of leaching solution containing ultra pure concentrated acids (0.1 mL concentrated HF and 0.4 mL 70% HNO_3). The leaching time was 15 hours for the natural, 20, 50, and 80% $^{235}U_3O_8$ samples, and 72 hours for the blank SNED sample. This variation is due to the overall concentration of uranium in the samples. The concenration of uranium in the blank SNED sample was significantly less than the other samples, as indicated by the uranium signal intensity obtained during LA-ICP-MS analysis. The blank SNED sample solution used in ICP-MS analysis used all of the leaching solution (0.5 mL) diluted with 30 mL of 2% HNO_3. A stock solution was made for the remaining samples using 50 µL of the leaching solution in 10 mL of 2% HNO_3. The stock solution was then diluted by a factor of 18 for ICP-MS analysis. For the solution analysis of the leached SNED samples, the ICP-MS parameters were optimized using Thermo Scientific Set Up solution. The dwell times were varied depending on the abundance of the isotope. If the isotope abundance was below 50% the dwell time was 100 ms, if the abundance was ≥ 50% the dwell time was 50 ms.

Table 2 Amount of SNED samples used in leaching study for solution isotopic analysis

Sample Name	Mass (mg)
Blank	32.5
Natural	13.7
20% U^{235}	11.6
50% U^{235}	7.9
80% U^{235}	6.3

Results and discussion

Synthesis of Material

Nuclear explosive melt debris from near-surface and underground detonations include diverse mixtures of glass, silicates, and subordinate oxides [5, 14-16]. The homogeneity of the melt glass after detonation ranges from glassy spheroidal aerodynamic fallout to ground glass which forms a smooth glassy surface transitioning to compositional variations of unmelted soil [5, 17]. Each sample of the SNED material was observed to have a white crystalline top (Figure 1 A) and greenish-blue transparent glass bottom with

inclusions of black (Figure 1 B), consistent with phases observed in ground glass samples of trinitite [18, 19]. The phase separation is either metal loading of the starting material, where two different liquid phases are more stable than one single phase during the melting process or incomplete melting of the starting material. However, the short melt time of one hour was successful in producing the desired heterogenous sample.

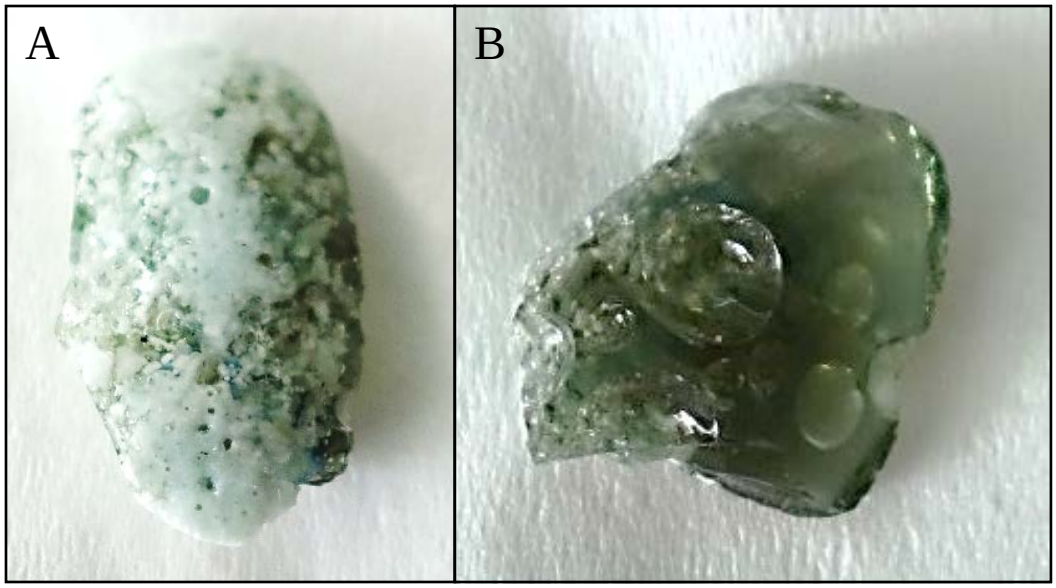

Fig. 1 Photos of SNED samples; A) White phase on top of samples, B) Greenish-blue phase on bottom of samples

The surface and cross section morphology of the SNED material was investigated using SEM. One of the natural uranium SNED fragments was mounted on its side to view a cross section of the glass shown in Figure 3 A-C. Vesicles, cracks, and pits were observed in the cross section as well as the surface of the green phase of the sample (Figure 3 E). The presence of internal cavities and pores are also observed in ground glass trinitite [19]. Conglomerates were visible on the surface of the white phase, shown in Figure 3 D. It is unclear if the conglomerates are a precipitate phase from the melting process, or if this phase is from incomplete melting of the starting material at various stages. The green phase was smooth (Figure 3 F) with surface bubbles (Figure 3 E) as previously mentioned. The vesicles and bubbles are due to volatile and low-boiling point elements being trapped in the melt during the cooling process. The morphology of the SNED samples are consistent with observations made with ground glass [19, 20] from the

Trinity test. The geometry of the furnace used in the melting process did not allow for quenching, which did not seem to affect the desired morphology of the SNED samples.

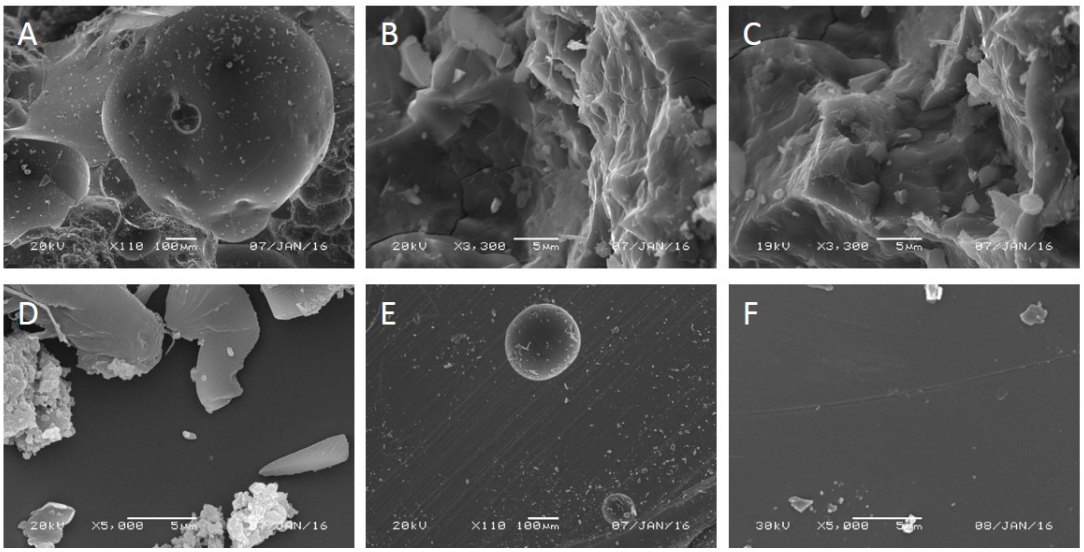

Fig. 2 SEM images of natural uranium SNED sample: A-C) Cross section images highlighting the internal cavities and pores, D) Surface image showing aggregates composing of the white top phase, E) Surface images of the bottom greenish-blue phase with surface bubble, and F) Smooth surface image of the bottom greenish-blue phase.

To determine the bulk elements of the white and green phases of the SNED samples, the blank SNED sample was analyzed using XPS. The limit of detection of XPS is assumed to be ≥ 0.1 atomic percent (at. %). The results of the XPS analysis are listed in Table 3, and were corroborated with EDS measurements. All of the elements detected in this analysis are assumed to be in their oxide form, and correlate with analysis performed on trinitite, with the exception of carbon [14, 21]. The temperatures of an actual nuclear detonation would result in carbon volatilizing within the cloud. The mass of the samples were measured before and after heating, where the average mass loss was found to be 12.9 ± 2.7 %. This mass loss is due to volatile and low-boiling point elements incorporated into the cement and soda lime raw material volatilizing during the melting process. Comparing the green phase of the melt glass to the white phase, overall the major elements are homogeneous with the exception of carbon and aluminum. There is significantly more carbon in the white phase and twice the amount of aluminum in the green phase than the white phase. The color of the white phase would indicate a

carbonate (either sodium or calcium) rather than elemental carbon. Calcium is a main component in the soda lime used in the synthesis and also present in Portland cement from the lime and limestone constituents. The remaining major elements, aluminum, magnesium, and iron are from the Portland cement used in the synthesis. Iron is incorporated into the cement via iron oxide pigment, where the aluminum is a main component of clay minerals. Magnesium is abundant in the earth's crust, therefore it could be incorporated into any of the constituents comprising the cement.

Table 3 Elemental compositon (at. %) of the green and white phases of blank SNED sample

	Atomic Concentration (at. %)	
Element	White Phase	Green Phase
C 1s	7.89	1.01
O 1s	55.66	59.81
Na 1s	3.86	2.81
Mg 2p	0.53	0.53
Al 2p	1.65	3.32
Si 2p	25.56	25.48
Ca 2p	4.68	6.7
Fe $2p_{3/2}$	0.16	0.34

To determine any trace constituents that may be an issue during nuclear forensic measurements of post detonation debric containing cement, a mass scan survey was performed using LA-ICP-MS. Three line scans from different areas of the 20% enriched ^{235}U SNED sample were investigated. Line scan ablations of the sample were 90 seconds in duration at 5 $\mu msec^{-1}$, with the instrument parameters listed in Table 1. A mass scan survey was collected from *m/z* 7-238. Comparing the natural abundance of each isotope with the signal intensity of the ICP-MS, element identification can be deduced. An example of this technique is shown in Figure 3 for barium. This technique was used to identify several elements found in the matrix but is more difficult for elements with only one isotope.

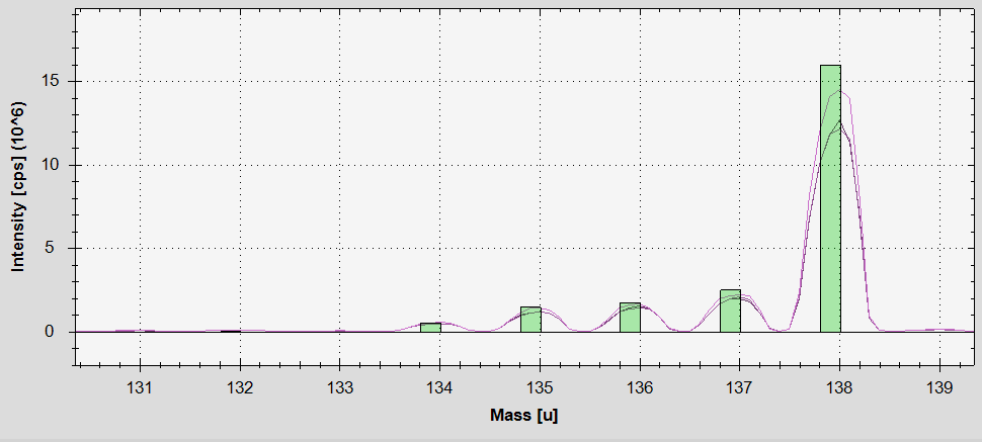

Fig. 3 Example of survey scan isotope fingerprint for barium, with the relative isotope abundance shown as green bars and the spectral data shown as the three red curves.

The minor and trace elements detected using LA-ICP-MS were a mixture of intermediate and refractory elements found in melt glass [22]. The signal intensities at the *m/z* measured are consisted with ppb to low ppm levels. Depending on the type of aggregate or binder used to make cement, trace and bulk elements will vary. Elements were identified to be equally distributed between the green and white phase include titanium, chromium, manganese, nickel, rhenium, and uranium . The well mixing of uranium in the SNED material is consistent with core samples analysis of underground nuclear explosive debris [14]. Table 4 lists the identified elements that were not homogenous between the green and white phases of the material. Since there are no standards for the trace elements for this matrix, a relative ratio of the signal intensities is reported. Rubidium, strontium, zirconium, and molybdenum lie in areas of interest in the thermal fission yield curve. Prior knowledge of materials may not be known in a post detonation scenario, resulting in a possible inaccurate nuclear forensic evaluation of the aftermath. For this reason, it is necessary to be able to accurately measure the isotope abundance of the fuel, for example uranium or plutonium, within the matrix. Polyatomic interferences such as PtAr, and PbO_2 can influence ^{235}U weight percent measurements [23, 24]. A significant amount of lead was detected in the green glass phase which could lead to inaccurate measurements of uranium isotopic ratios. Due to the possibility of lead and platinum incorporation in a post-detonation scenario in an urban environment, survey scans of the melt glass would be essential in determining interferences and areas of interest to accurately measure the

isotope abundance of the fuel used in the device for LA-ICP-MS analysis. The use of a collision cell would also mitigate polyatomic interferences.

Table 4 Ratio of the signal intensities of trace elements detected in 20% ^{235}U SNED sample results from LA-ICP-MS analysis

Element	Cu	Zn	Rb	Sr	Zr	Mo	Ba	Ce	W	Pb
Green/White	0.090	2.481	1.551	1.458	0.606	0.066	2.480	1.646	0.186	5.524
Std. Dev.	0.002	0.790	0.168	0.093	0.080	0.008	0.104	0.217	0.026	0.590

Uranium Isotopic Ratio Measurements using LA-ICP-MS

Laser ablation ICP-MS analysis has been used in literature to evaluate SNED and trinitite extensively, [8, 18, 21, 25-28] but is not listed as an analytical tool for nuclear forensics by the IAEA [12]. However, the IAEA includes ICP-MS as an analytical tool for nuclear forensics to determine isotopic and elemental concentrations in samples. A side by side comparison of the uranium isotope measurements was performed with LA-ICP-MS and ICP-MS on the SNED samples to determine the viability of using LA-ICP-MS in a post-detonation scenario. The same ICP-MS was used for both sample introduction methods, keeping the detector variability constant and comparing sample introductory techniques. The laser ablation sampling techniques include spot, line scan, and depth profile analysis. Each sampling technique evaluated the white side of the material to avoid polyatomic intereferences from PbO_2 abundance in the green phase, detected during the mass scan survey. These techniques are looked at to determine if the small sampling area is representative of the bulk material, but also highlight the spatial resolution of laser ablation.

The depth profile sampling method was performed using LA-ICP-MS to determine the homogeneity of the uranium isotope ratio within the sample. The method drilled down into the sample with sequential laser shots, decreasing in spot size from 110 μm to 40 μm in increments of 10 μm. The variation in spot size was designed to ensure that the laser-sample coupling was consistently at the bottom of the crater, rather than the sides of the crater, due to re-solidification during the ablation process. The depth measurements reported in Figure 4 are estimated from a separate experiment where the laser was focused within the crater between samplings. The average depth of sampling was found

to be 18.6 ± 0.7 μm for a total change in depth of 139.0 ± 4.2 μm. The isotopic measurements from the focusing study were found to be the same as the measurements without refocusing indicating that focusing the laser between measurements is not needed for this system. The distance between measurements most likely falls within the depth of focus in regards to the beam waist of the laser. In the graphs shown in Figure 4, the horizontal line denotes the theoretical value for each sample. Overall the samples appear to be homogenous with depth as shown, and the blank SNED sample has the most variability of the isotope ratio measurements with regards to depth. The high standard deviation for the drill down method analysis of the blank sample can be explained by the surface morphology, and due to the stationary nature of the sampling method. If the area chosen is next to a pit/void in the sample the laser contact with the surface is compromised, where the laser energy is not uniformly absorbed by the surface.

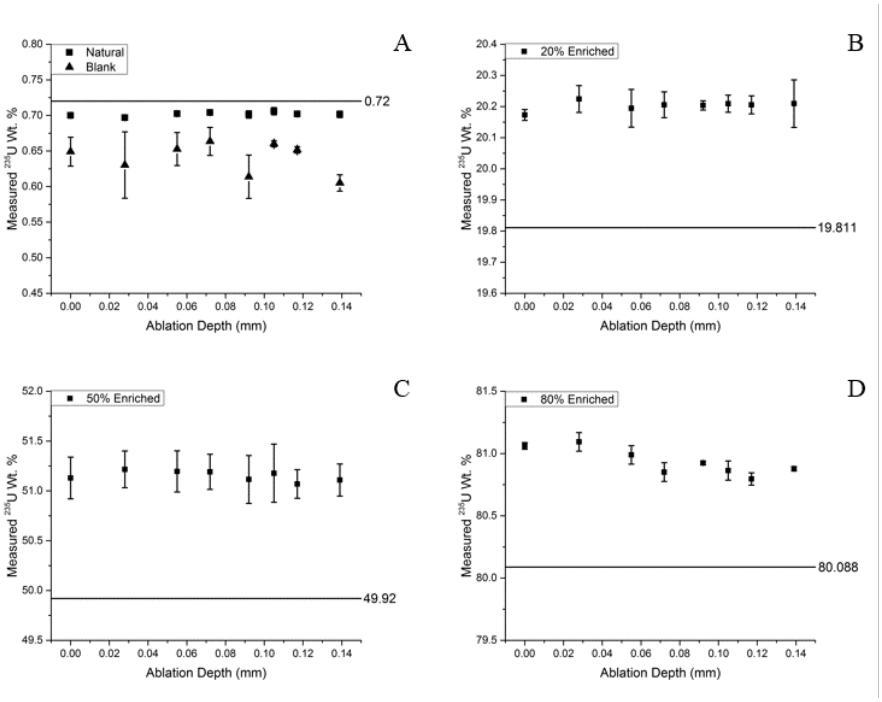

Fig. 4 LA-ICP-MS depth analysis of the SNED samples at varying enrichments. A) Blank and natural, B) 20% enriched ^{235}U, C) 50% enriched ^{235}U and D) 80% enriched ^{235}U

The analysis of the blank SNED sample revealed a higher than expected abundance of uranium. These samples were prepared to simulate environmental samples and are therefore accurate in terms of the blank containing some level of uranium. The source of

the uranium detected in the blank sample is most likely from the aggregates used in the concrete material, where the concentration of uranium can vary significantly depending on the ore body. In order to quantify the amount of uranium in the blank, the second set of uranium doped glass samples prepared by LLNL were used as standards for LA-ICP-MS analysis. The linear correlation value (R^2) for both the ^{235}U and ^{238}U calibration curves were found to be 0.999. When quantifying uranium using LA-ICP-MS, it is important to use standards that have relatively the same isotopic abundances of ^{235}U and ^{238}U. Although the calibration curves are isotope specific, they determine the overall elemental concentration. The total concentration of uranium in the blank sample was found to be 3.68 ± 0.12 ppm and 3.42 ± 0.09 ppm for ^{235}U and ^{238}U calibration curves, respectively. The variation in the quantification measurement between ^{235}U and ^{238}U is most likely due to the lower isotopic ratio of the blank sample (0.66) in relation to the standards (0.72) used to make the measurement. This will result in an artificial increase of the ^{235}U concentration and decrease of the ^{238}U concentration as shown in the measurement. The actual uranium concentration in the sample is likely to be some value between 3.42 ± 0.09 ppm and 3.68 ± 0.12 ppm.

Each sampling technique is evaluated for accuracy and precision by calculating the percent bias and the percent relative standard deviation (RSD), respectively. The results of the accuracy and precision of the measurements are listed in Table 5. Corrections for mixing of two different uranium sources has been described elsewhere, [5, 18] so it will not be addressed in this analysis. Therefore, the relative accuracy of the measurement is compared for the sampling methods. The blank and natural SNED samples measured values are significantly lower than the expected theoretical value for all of the sampling techniques tested, with the highest percent bias values calculated for the sample series. Since the sources of uranium used in the blank and natural samples are not certified material, the assumption that they are purely natural may not be true. For the enriched samples, the depth profile sampling method has the highest deviation from the certified values, in regards to the accuracy of the isotopic ratio measurement. The measured values for the enriched samples of all the sampling methods, except the line scan analysis, are greater than the theoretical values. The line scan LA-ICP-MS sampling method percent bias values are within statistical error of the solution phase ICP-MS analysis. This

suggests that the line scan analysis sampling method is just as accurate as solution phase ICP-MS analysis for determining the bulk isotopic ratio of the material without needing to digest the sample.

The precision of each sampling method is evaluated by comparing the percent RSD values. The sampling method that resulted in the most precise measurement of the blank and natural isotope ratios was the LA-ICP-MS line scan analysis. The precision of all the sampling methods for the enriched samples fall below 0.5 % RSD, where the depth profile sampling method is the most consistent of solid sampling methods for the enriched samples. The performance of each solid sampling technique in regards to precision of the measurement will depend on the surface morphology and geometry of the sample. It is recommended that an optimization of the sampling technique be performed for each type of sample (soil, glass, etc.) when using LA-ICP-MS as a nuclear forensic analytical tool.

Table 5 Solid (LA-ICP-MS) and solution phase (ICP-MS) analysis of the SNED samples at varying enrichments of uranium

Theoretical ^{235}U Wt. %	**Sampling Technique**	**Measured ^{235}U Wt. %**	**% Bias**	**Wt. % Std. Dev.**	**Wt. % RSD**
0.72 (Blank)	Line Scan	0.635	-11.8	0.002	0.26
	Spot	0.685	-4.8	0.015	2.20
	Depth Profile	0.641	-11.0	0.022	3.40
	Solution	0.668	-7.3	0.003	0.41
0.72 (Natural)	Line Scan	0.689	-4.3	0.001	0.18
	Spot	0.685	-4.8	0.002	0.31
	Depth Profile	0.702	-2.5	0.003	0.38
	Solution	0.685	-4.8	0.002	0.26
19.811	Line Scan	19.702	-0.6	0.014	0.07
	Spot	20.047	1.2	0.049	0.25
	Depth Profile	20.203	2.0	0.015	0.07
	Solution	20.008	1.0	0.010	0.05
49.92	Line Scan	49.635	-0.6	0.131	0.26
	Spot	50.413	1.0	0.018	0.04
	Depth Profile	51.150	2.5	0.052	0.10
	Solution	50.213	0.6	0.018	0.04

80.088	Line Scan	79.922	-0.2	0.171	0.21
	Spot	80.916	1.0	0.033	0.04
	Depth Profile	80.932	1.1	0.106	0.13
	Solution	80.247	0.2	0.008	0.01

Conclusions

The synthesis of SNED samples was successful in producing samples that were similar to ground glass trinitite in both chemical heterogeneity and morphology characteristics. The melting temperature and profile resulted in a two phase glass that had vesicles, cracks, and pits. The urban matrix was shown to be complex resulting in minor and trace elements that can obscure nuclear forensic calculations necessary to answer key questions including yield, sophistication of the device, and provenance of materials. Lead was also detected in significant quantities that could affect uranium isotope measurements using ICP-MS or LA-ICP-MS without sample treatment, due to polyatomic interferences of PbO_2. Polyatomic interferences can be limited with the use of an ICP-MS that contains a collision cell. Samples with complex spatial and chemical heterogeneity such as these would be beneficial to the nuclear forensics community for measurement exercises, training, and method development of analytical techniques.

This work also explored the use of LA-ICP-MS for quantitative isotopic analysis of uranium, concentration of uranium, and qualitative determination of minor and trace constituents found in the SNED samples. The soda lime and cement uranium SNED samples isotopic composition was analyzed by LA-ICP-MS and compared with the leached analysis using solution phase ICP-MS. Within the solid sample analysis, LA-ICP-MS, the samples were investigated for homogeneity using line scan, depth profile and spot laser sampling. The samples were found to be homogeneous with regards to surface and depth analysis of uranium concentration and isotope ratios. All of the sampling techniques including solution analysis of the leached glass measured values for the blank and natural samples are significantly lower than the expected theoretical. Since the sources of uranium used in these samples are not certified material, the assumption

that they are purely natural may not be true. Thermal Ionization Mass Spectrometry measurements of the uranium isotopes would be needed to verify the theoretical values assumed in this work are correct. The results for each LA-ICP-MS sampling method compared very well with solution phase ICP-MS. This demonstrates that LA-ICP-MS is a rapid technique for post-detonation analysis with percent bias within statistical error of solution analysis and reasonable precision. Using LA-ICP-MS in a post-detonation scenario is beneficial in providing answers to key questions in a more timely fashion than solution phase ICP-MS.

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Supplemental

Two sources of 20% and 80% enriched $^{235}U_3O_8$ were down-blended to produce a third source of 50% enriched $^{235}U_3O_8$. The desired masses of the two enrichments, (50.8 mg of 20% $^{235}U_3O_8$, and 50.7 mg of 80% $^{235}U_3O_8$), were added to 10 mL of ultra-pure concentrated nitric acid from JT Baker to dissolve the oxides. The solution was then heated to 100˚C for 15 minutes and then cooled to room temperature for 1.5 hours. De-ionized water (15 mL) was added to the solution, followed by 20 mL of concentrated ammonium hydroxide saturated in oxalate. The container was then placed in an ice bath for 10 minutes as the reaction is exothermic. The solution was then vortexed for 2 minutes followed by centrifugation at 2500 rpm for 5 minutes. The solution was then decanted and the precipitate was freeze dried overnight. The precipitate was then calcined at 200 ˚C for 2 hours, 500 ˚C for 2 hours, and 600 ˚C for 12 hours in ambient air to produce 50% enriched $^{235}U_3O_8$. Powder x-ray diffraction was performed on the sample for phase identification and confirmed the 50% enriched $^{235}U_3O_8$ was α-U_3O_8.